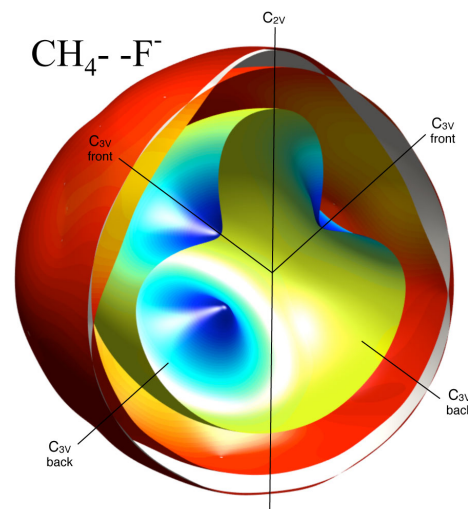


THE JAHN-TELLER EFFECT AS A TREATMENT OF MOLECULAR ANHARMONICITY

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An important aspect of vibrational anharmonicity results from the substantial changes in molecular geometry and bonding that occur in the coordinate space of large-amplitude nuclear motion. Examples of such large-amplitude motion include torsional motion, inversion, the intermolecular motions within clusters, and reaction coordinates. Here we show that the Jahn-Teller formalism, when suitably extended, provides a precise description of the variation of the small-amplitude vibrational frequencies in a large-amplitude coordinate space. The locations where the small-amplitude frequencies cross are vibrational conical intersections (CIs) and multiple CIs may occur in one molecular system. In this work, we expand the motion of one molecular fragment relative to the other in spherical harmonics to allow an even-handed treatment of large-amplitude motion in 4π steradians. The molecular systems treated include CH_3OH , CH_3SH , and the complexes of CH_4 with F^- and Na^+ ions. The Jahn-Teller formalism provides a general treatment of near-resonant interactions including their explicit dependence on large-amplitude nuclear coordinates. It also includes a crude adiabatic basis, which allows for convenient computation of the fully coupled quantum nuclear dynamics. The opportunities and limitations of this approach will be discussed.



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